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CONTENTS

CONDUCTIVITY STUDY ON PLASTICIZED CHITOSAN ACETATE BASED ELECTROLYTES DOPED WITH SILVER TRIFLATE SALT SYSTEM

A.M.M. Ali[a]*, M.Z.A. Yahya[a], M.K. Harun[a] and A.A. Mohamad[b]

[a]*Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.*
[b]*School of Materials and Mineral Resources Engineering,Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia.*

**Corresponding author: Tel : +603-5544 4496, Fax : +603-5544 4562*
email : ammali@salam.uitm.edu.my

ABSTRACT

Plasticized polymer electrolytes composed of chitosan as the host polymer, ethylene carbonate (EC) as the plasticizer and silver triflate ($AgCF_3SO_3$) as the doping salt were prepared by the solution cast technique. These complexes with different amounts of salts and plasticizers were investigated as possible ionic conducting polymers. This salt was chosen based on the ability of silver cation to exist as monovalent cation, which could influence the mobility of the ions in the chitosan-based electrolytes. The highest electrical conductivity, σ for the chitosan-silver triflate salt at room temperature was 1.0 x 10^{-5} S cm^{-1}. Conductivity for the plasticized $AgCF_3SO_3$ (Ag Tf) doped chitosan polymer was also studied as a function of temperature between 300 K and 363 K. The plot of $\ln(\sigma T)$ versus $10^3/T$ for each sample obeys Arrhenius rule indicating the conductivity to be thermally assisted. The activation energy, E_a was calculated from the Arrhenius plots and the increase in conductivity can be explained in terms of the decrease in E_a and vice versa. The highest conducting CA-EC-$AgCF_3SO_3$ complex has the lowest E_a of 0.60 eV. FTIR spectroscopy and XRD techniques were carried out for the complexation studies.

Keywords: solid polymer electrolytes, chitosan, electrical conducting polymer, plasticizer

1. INTRODUCTION

The first polymer observed to have the ability to solvate inorganic salt was polyethylene oxide, (PEO)[1]. The electrical conductivity of this salt-solvating polymer has been measured[2-3]. The technological significance of this polymer was recognized only in 1978 when Armand[4] announced the existence

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of a material capable of dissolving salt to form a novel class of ionic conductors. Since then, many new complexing polymers have appeared, in the search for ion conducting polymers with higher room temperature electrical conductivity. The main objective of this work is to establish chitosan as an ionic conducting polymer with doping of silver triflate salt. One of the criteria to establish a polymer as an ionic conductor is that the polymer must be able to solvate the salt. A polymer is said to solvate the salt if there is direct interaction between the lone pair electrons of a heteroatom such as oxygen or nitrogen in the polymer and cations of the salt. In chitosan, the nitrogen atom in the amine functional group and the oxygen atom in the hydroxyl functional group each bears lone pair electrons. The cation of the inorganic salt will form a dative bond with the oxygen or nitrogen and hence a chitosan-salt complex is formed. However, other investigations, also quoted from the same reference have demonstrated that large amounts of salt from group IA metals do not produce any appreciable alterations on chitosan[5-6]. If there is no interaction between the doping salt and the lone pair electrons of the nitrogen atom in the amine group, then the criteria for a polymer host to become successful polymer electrolytes will be violated. Hence, in order to establish chitosan as an ionic conducting polymer, we have to show that complexation will occur between the heteroatom in chitosan and silver salt. Thus, the existence of lone pair electrons on the nitrogen atom is the main driving force pushing studies on new applications, particularly as electrochemical cells, of this biopolymer.

2. EXPERIMENTAL METHODS

Chitosan powder used in the present investigation was obtained from Fluka. All samples were prepared by solution casting technique. Chitosan with 6.0 x 10^5 g mol^{-1} molecular weight was used. A stock solution of composition 1.0 g chitosan in 100 ml 1 % of acetate acid was prepared. The inorganic salt, recrystallized silver triflate (Ag Tf) was taken in different stoichiometric ratios and dissolved in the stock solution. The mixtures were continuously stirred with a magnetic stirrer for several hours at room temperature to ensure complete dissolution of the salt. To enhance the conductivity, 0.40 g of ethylene carbonate (EC) was added to each solution as a plasticizer. The amount of EC added was in accordance to previous work[7] which showed that the film prepared from evaporating a solution containing 1.0 g chitosan and 0.4 g EC dissolved in 100 ml of 1% acetic acid solution exhibited the highest electrical conductivity. The prepared solutions were then cast into different plastic petri dishes and the films were allowed to form at room temperature. The films took about several weeks to form. The resulting films were then kept dry in a dessicator for further experiments.

In this study, the samples of plasticized chitosan acetate-salt with EC were characterized by X-ray diffraction (XRD)

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to study the effect of the dissolution of the salt on the structure of the polymer. Fourier transform infrared (FTIR) spectroscopy was carried out to double-check the occurrence of complexation between salt and polymer. The electrical conductivities of all samples were measured by impedance spectroscopy technique.

3. RESULTS AND DISCUSSION

XRD patterns of all samples are shown in Figure 1. The XRD spectrum of pure chitosan acetate (CA) shows that the sample is partly crystalline with peaks at θ = 10.5°, 16.0° and 18.0°. Upon addition of 0.40 g of EC, it can be observed that the sample has become more amorphous[8]. The addition of plasticizer disrupts the crystalline nature of the chitosan acetate film. On the addition of 0.10 g silver triflate, the peaks attributed to chitosan acetate and EC in the range $10° < 2\theta < 20°$ disappear but the peaks at 2θ = 30° and 45° remain and are slightly shifted showing some degree of complexation. On the addition of 0.20 g silver triflate, a totally amorphous phase exists. When more than 0.20 g silver triflate is added the films become crystalline again. Thus XRD is able to show complexation in chitosan-silver salt system but is not powerful enough to prove complexation.

FTIR was carried out to justify the occurrence of chitosan-salt complexation. The infrared spectra of the CA and CA-EC samples are shown in Figure 2 (a) & (b) respectively. It is quite obvious that the spectrum for CA is almost similar to that of the CA-EC film implying that EC acts as a lubricant. Figure 2 depicts the spectra of CA, CA-EC and the plasticized polymer-salt films. The spectrum of chitosan is similar to that given by Muzarelli[9]. The distinct band at 1590 cm^{-1} is the amine band. The position of this band is shifted to lower wavenumbers at 1575 cm^{-1} indicating that some complexation has occurred either between the salt and the nitrogen atom of the amine group or between acetic acid and the nitrogen atom. However, as more salt is doped to the solution, the shift increases further towards lower wavenumbers. This implies that complexation does occur between the salt and chitosan. According to Schrader[10], triflate anion has a band at wavenumbers 1272 cm^{-1} and 1223 cm^{-1}, which are due to the bands of SO_3 and CF_3 respectively. Upon addition of silver triflate to the plasticized chitosan acetate, two bands can be observed at ~ 1280 cm^{-1} and 1255 cm^{-1}. This can be inferred that there is some interaction between sulfonate anion with chitosan acetate. As a result the sulfonate band is shifted from wavenumbers 1272 cm^{-1} to ~ 1280 cm^{-1} and chitosan acetate band is shifted from wavenumbers 1260 cm^{-1} to 1255 cm^{-1}.

Three main peaks were observed at wavenumbers 1650 cm^{-1}, 1580 cm^{-1} and 1555 cm^{-1} which due to the vibrations of O=C-NHR, NH_2 and NH_3^+ as shown in Figure 2 (a) and (b). These peaks are observed to have shifted to lower wavenumbers due to the formation of the chitosan-acetate acid salt where the

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hydrogen of the acetic acid has formed a dative bond with the nitrogen of the NH_2 group. The shifting of these peaks particularly the NH_2 peak also depends on the types of cation interacting with chitosan acetate, the type of counter anion and their concentration[5]. If complexation occurs between the silver ion and the nitrogen atoms in the chitosan structure, there should be further shifting and possible overlaps between the NH_2 and NH_3^+ bands. This can be clearly observed in the spectra represented in Figure 2 (d) to (i). Upon closer examination, the whole spectra tend to shift to lower wavenumbers as the salt content is increased. Hence it can be inferred that complexation between the silver ions and the nitrogen atom of the amine (NH_2) group has taken place and the chitosan film can be considered as a successful polymer host for the dissolution of the silver triflate salt. Complexation between chitosan-salt will increase the amorphous regions in the samples. According to Linford[11], Ag^+ ions exist in the amorphous regions with comparable mobility and contributes to the electrical conductivity.

From Figure 3, it can be observed that the conductivity of the complexes increases with content of the doping salt and reaches a maximum value of 1.0×10^{-5} S cm^{-1} in the sample containing 0.20 g of the silver salt. The increase in the conductivity is attributed to the increase in the number of free mobile ions. The electrical conductivity decreases upon further addition of salt as a result of the formation of neutral ion pairs[12].

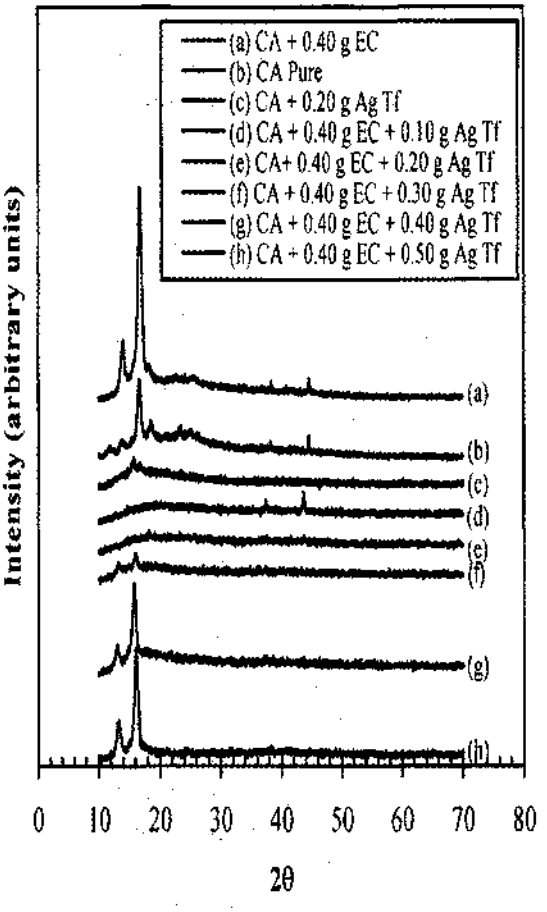

Figure 1: XRD patterns for all samples: plasticized chitosan acetate (CA-EC), chitosan acetate pure, chitosan acetate doped with 0.20 g silver triflate (Ag Tf) and plasticized chitosan acetate doped with various concentrations of silver triflate.

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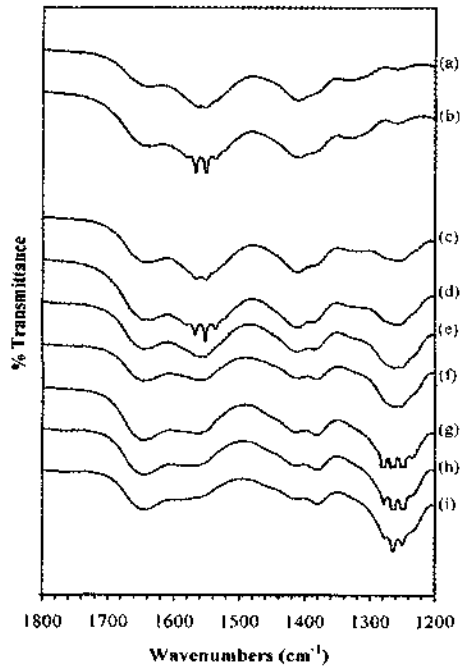

Figure 2: FTIR spectra of (a) CA + 0.40 g EC (b) CA pure (c) CA + 0.40 g EC + 0.10 g Ag Tf (d) CA + 0.40 g EC + 0.20 g Ag Tf (e) CA + 0.40 g EC + 0.30 g Ag Tf (f) CA + 0.40 g EC + 0.40 g Ag Tf (g) CA + 0.40 g EC + 0.50 g Ag Tf (h) CA + 0.40 g EC + 0.60 g Ag Tf (i) CA + 0.40 g EC + 0.70 g Ag Tf.

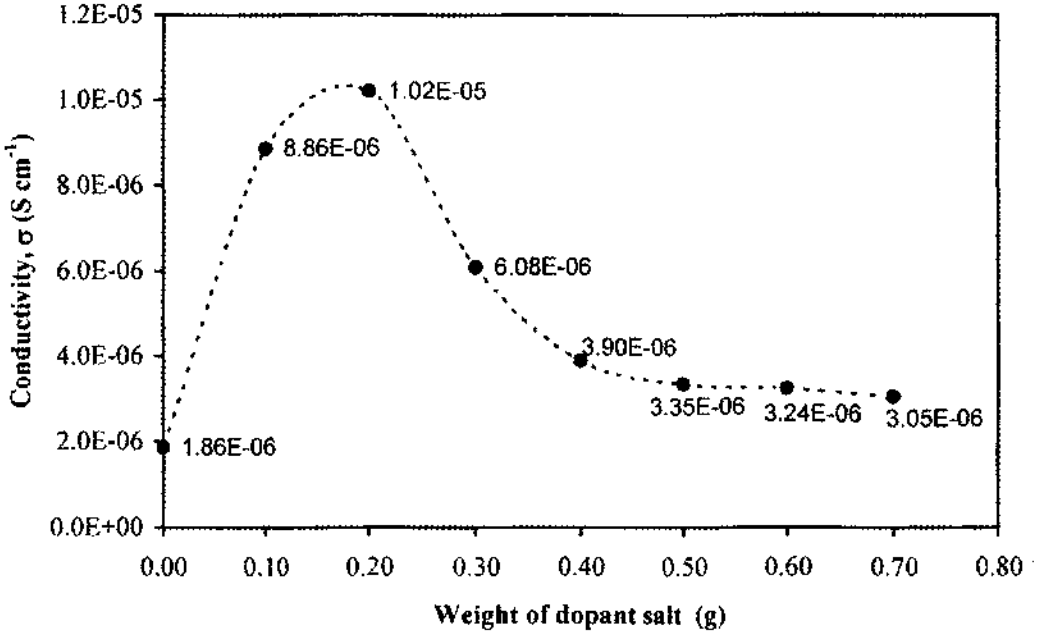

Figure 3: Variation of electrical conductivities of pure chitosan acetate and plasticized chitosan acetate versus various amount of dopant Ag Tf at room temperature.

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The information given in Figure 4 suggests that electrolyte displays Arrhenius behavior in the temperature range studied and that the conductivity occurs by a thermally assisted transport process[13]. It can be explained that if the conductivity-temperature data follows the Arrhenius relationship below T_g, the conductivity mechanism is quite similar to that occurring in ionic crystals where ions (produced by thermal agitation) jump into the neighboring vacant sites. The same explanation seems plausible in the case of the present investigation.

Figure 5 shows that the activation energy of the samples is in inverse relationship with the conductivity values. It can be observed that the activation energy is the lowest when the electrical conductivity is the highest (Figure 3). Hence, this can be inferred that the completely amorphous nature of the polymer electrolytes facilitates the fast Ag^+ motion in the polymer network and it further provides a larger free volume in the polymer electrolyte system upon increase in temperature[14].

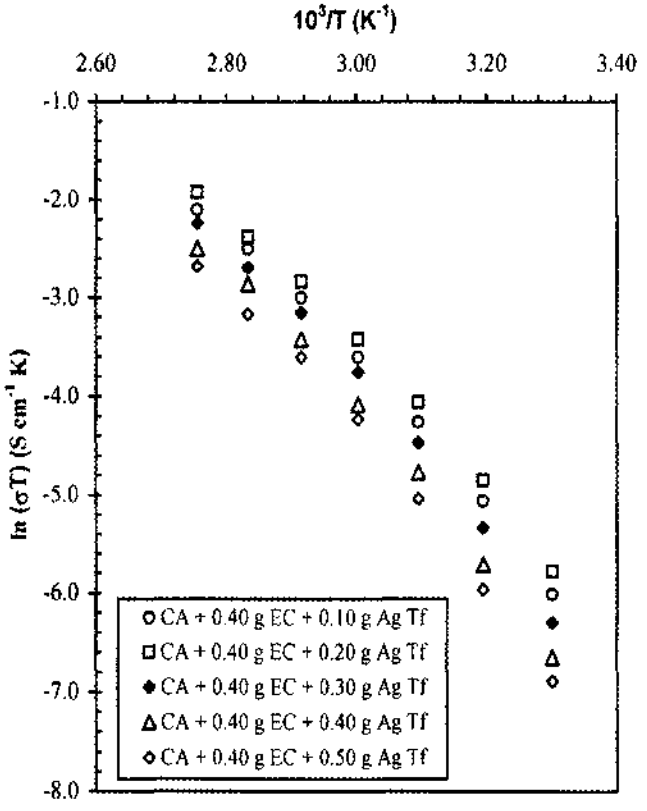

Figure 4: Arrhenius plots of plasticized chitosan acetate doped with various weights of Ag Tf.

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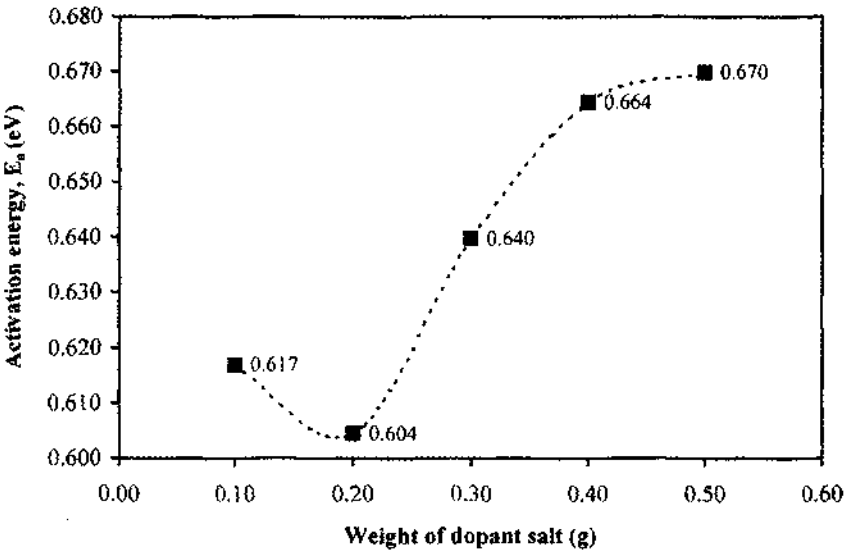

Figure 5: Activation energy versus various amounts of dopant content.

4. CONCLUSION

Chitosan-silver triflate salt complexes have shown to behave as ionic conductors. The highest electrical conductivity at room temperature is 1.0×10^{-5} S cm^{-1} for the sample containing 0.20 g of silver salt in CA-EC system. The value of activation energy is 0.604 eV. It can be inferred that the polymer electrolytes facilitates the fast Ag^+ motion in the polymer network and it further provides a larger free volume in the polymer electrolyte system upon increase in temperature. The conductivity that has been obtained by adding $AgCF_3SO_3$ and EC to chitosan makes this material a potential candidate in some electrochemical devices such as silver ion batteries and silver-based humidity sensors.

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